

Doklady Akad. Nauk SSSR 104, 260-3 (1955)STRUCTURE OF SOME CRYSTALLINE ORGANOLITHIUM
COMPOUNDS. TERNARY COMPLEXES

By

T.V. Talalaeva and K.A. Kocheshkov

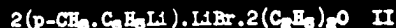
During a systematic study of conditions of formation, structure and properties of organo-alkali metal compounds, in particular during the study of their individual crystalline habits, the authors have noticed that, upon action of lithium on bromobenzene in ether, the resulting crystalline solid has a more complex character than indicated by the formula C_6H_5Li .

This observation is of importance first because the direct action of the metal on the alkyl or aryl halides is one of the principal methods of synthesis of organo-lithium compounds, and secondly because it is closely associated with the question of structure of Grignard complexes, the study of which, during the several decades (1900-1930) has shown their considerable complexity.

Actually, as the authors have shown^{1,4}, and have experimentally proven, the structure of organo-lithium compounds, described in this article, shows a definite analogy with the organo-magnesium complexes, and have an aryl metal or an alkyl-metal, a metal halide and ether as the complex components.

The existence of lithium bromide monoetherate, $LiBr(C_2H_5)_2O$, described by the authors in this article for the first time, even further supports the above mentioned analogy to the organo-magnesium complexes. **

Finally, the marked difference between the authors' data and the results of B.M. Mikhailov and N.G. Chernova⁵, and the impossibility of duplicating their experimental methods of preparing phenyl lithium monoetherate from bromobenzene and lithium in ether, has prompted the authors to investigate other methods of preparation of the complex. From the detailed experimental data and chemical analyses offered below it can be seen that in the direct reaction between bromobenzene (or p-bromotoluene) and lithium in ether solution the crystalline reaction products that separate out have the following complex compositions, corresponding to formulas I and II.



* Naturally the structure of organo-lithium compounds, as a univalent metal does not include the type analogous to R_3MX .

** The authors also obtained lithium iodide monoetherate

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According to Mikhailov and Chernova², however who, it seems have missed during their analyses about 20 percent lithium bromide, the complex should have the following composition:



For more complete proof of the structure of the ternary complexes of lithium, the authors have developed another independent synthetic method of their preparation, by reaction of crystalline phenyl-lithium (or p-tolyl-lithium) with excess lithium bromide (or more exactly its monoetherate) in ether solution. The resulting crystalline solids were analyzed. Their analysis showed them to correspond to the compositions represented by I and II. In this manner two independent methods of preparation lead to the same complex ternary lithium composition.

The isolation of these ternary complexes does not exclude the possibility of obtaining individual RLi, as was first shown by Schlenk³, and further developed by the authors on the basis of perfected methods of preparation, as described in^{1,4} as well as the possibility of obtaining the RLi etherates, as described by Gross⁵.

Undoubtedly, the composition of the above discussed ternary complexes depends on their solubility, temperature, subsequent treatment, etc. The above mentioned lithium bromide monoetherate was prepared according to the following equation:



The above reaction was carried out in ether. The monoetherate is quite soluble in ether even at -10°C at normal concentrations. This fact explains the absence of its solid phase during the interaction of organic bromides with lithium in ether. The authors point out, that in the recent work of A.N. Komendantov, A.R. Barisov and N.V. Novikova⁷ there was no need to resort to a hypothetical complex of isopropenyl-lithium with lithium bromide. Also in the same work, there is a faulty indication that during the reaction of n-butyl bromide with lithium in ether, the lithium bromide appears as a solid phase. The author's data indicate that under normal conditions, essentially all lithium bromide remains in solution.

Experimental

All of the experimental procedures were carried out in the atmosphere of dry nitrogen, in a special apparatus, described in author's previous communications, using carefully dried reagents.

Preparation of $2\text{C}_6\text{H}_5\text{Li} \cdot \text{LiBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ from Bromobenzene and Lithium in Ether

A. Solution of phenyl lithium is obtained, as usual from 31.4 grams of bromobenzene (0.2 moles) and 3.35 grams of lithium (0.4 moles + 20% excess) in 120 ml. of diethyl ether. After standing overnight the solution was found to be 1.137 N with respect to phenyl lithium and 1.366 N with respect to lithium bromide. Diethyl ether is then partially removed by distillation - 15 ml of ether are removed from

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50 ml of clear solution. Upon cooling the concentrated solution in ice, a quantity of transparent needle crystals separates out of mother liquor (with a small amount of heavy sediment found on the bottom of reaction flask). Upon reheating, the needle-like crystals dissolve, and the solution is allowed to stand for 10-15 minutes. The clear solution is then decanted off to another vessel and is again cooled with ice. The resulting needle crystals are filtered off using a fritted glass filter and then are dried in a small stream of dry nitrogen until they stop adhering to the sides of the filtering vessel. The dried crystals are transferred to a tared ampule and weighed. For analysis a weighed sample is transferred from an ampule to a small flask containing 10-15 ml of dry benzene. It is then slowly decomposed first with small portions of ethanol, then with water. For analytical data, see Table IA.

B. In carrying out the reaction under conditions specified by B.M. Mikhailov and N.B. Chernova² for preparation of "phenyl lithium monoetherate" - 1.3 grams lithium, 15 grams bromobenzene in 30 ml of diethyl ether - after cooling to room temperature and standing overnight - a dark liquor is obtained with a considerable amount of heavy whitish sediment, interspersed with transparent white crystals. Upon reheating of the reaction mass, the transparent crystals are redissolved, the clear liquor is decanted off into another vessel and cooled again. The transparent needle like crystals are filtered and dried as described above. Analysis of the dry product is shown in Table IB.

Thus, even under these conditions of higher concentration of reactants, crystals of the ternary complex are obtained, corresponding almost exactly (within the limits of experimental error) to solids obtained in test A (and not the mono-etherate $C_6H_5Li(C_6H_5)_2O$).

Table I

	Sample Weight	Ml. 1N H_2SO_4	Ml. 1N $AgNO_3$	C_6H_5Li or $CH_3C_6H_4Li$ percent	LiBr percent	Ether by diff. percent	Mol. ratios		
A	0.2219	11.12	5.28	42.06	20.67	37.27	2	0.95	2.01
	0.2338	11.71	5.47	42.04	19.86	38.10	2	0.91	2.05
B	0.2127	10.53	4.91	40.77	20.05	39.18	2	0.94	2.17
	0.2293	11.20	5.32	41.00	20.15	38.85	2	0.93	2.14
C	0.4112	19.90	9.72	40.62	20.52	38.86	2	0.97	2.16
	0.4848	23.30	11.63	40.34	20.83	38.83	2	0.99	2.18
D	0.2142	10.01	4.83	46.20	19.58	34.22	2	0.96	1.96
	0.1871	8.70	4.25	45.57	19.73	34.70	2	0.97	2.01
E	0.3036	14.30	7.30	46.16	20.88	33.96	2	1.02	1.95
	0.2904	13.63	6.90	45.99	20.64	33.37	2	1.01	1.91

Analysis of the heavy whitish solid sediment shows it to be a mixture of lithium bromide, a concentrated solution of phenyl lithium and finely divided lithium metal.

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C. Preparation of $2C_6H_5Li \cdot LiBr \cdot 2(C_6H_5)_2O$ from crystalline phenyl lithium and in ether solution of lithium bromide.

Crystalline phenyl lithium was obtained from 350 ml of 0.815 N benzene solution of ethyl lithium (0.28 moles) and 43.9 grams (0.28 moles) of bromobenzene at room temperature, standing overnight, in a quantitative yield. The crystalline precipitate (24.79 grams, 0.28 moles), containing a small amount (5-5%) of lithium bromide, which, as pointed out in author's earlier work results from the exchange reaction with bromobenzene, was filtered off, washed with isopentane, dried in a stream of dry nitrogen and then dissolved, with slight heating, in 25 ml of diethyl ether. To the resulting solution, 125 ml of 1.65 N ether solution of lithium bromide (see below) - 17.9 grams LiBr, 0.2 moles - are added. The resulting solution is then filtered through a fluted paper filter to get rid of a slight turbidity. The clear filtrate is concentrated by removal of 100 ml of diethyl ether by distillation. Upon cooling in ice, a large crop of beautifully formed needle crystals almost fills the total volume of the solution. These are filtered off on a fritted glass filter and dried for 45 minutes in a small sweep of dry nitrogen. The dry crystals are then analyzed. The analytical data are listed in Table I, C. Since in this preparation LiBr was added in definite excess, the filtrate from this preparation is enriched with it (the ratio of C_6H_5Li to LiBr in filtrate is approximately 2:3).

D. Preparation of $2p\text{-CH}_3\text{C}_6\text{H}_4Li \cdot LiBr \cdot 2(C_6H_5)_2O$ from p-bromotoluene and lithium bromide in ether solution

A solution of p-toluyllithium was prepared from 34 grams (0.2 moles) of p-bromotoluene and 3.35 grams (0.4 moles + 20% excess) of lithium in 200 ml diethyl ether. After standing it was found to be 1.302 N with respect to p-toluyllithium and 1.368 N in lithium bromide. This solution was concentrated by distillation of ether (15 ml of ether removed for every 50 ml of solution). The resulting concentrated liquor was cooled to -20°C. Crystallization of small needle like crystals was induced by agitation and scratching with a glass rod. These crystals were filtered and dried as described previously in case of phenyl lithium derivatives. The analytical data are shown in table I, D.

E. Preparation of $2p\text{-CH}_3\text{C}_6\text{H}_4Li \cdot LiBr \cdot 2(C_6H_5)_2O$ From Crystalline p-Toluyllithium and Lithium Bromide in Ether Solution

Crystalline p-toluyllithium was obtained from 100 ml of 1.41 N benzene solution of ethyl lithium (0.14 mole) in 23.9 grams (0.14 moles) of p-bromotoluene after standing overnight. The resulting precipitate is filtered, washed twice with isopentane and dried in the dry nitrogen sweep (yield 10.2 grams include 15% lithium bromide impurity). These solids are dissolved in 70 ml of 1.65 N ether solution of lithium bromide (0.11 moles), at the boiling temperature of diethyl ether (only a small, heavy sediment remains undissolved). The resulting liquor is then concentrated by distillation of diethyl ether until a 30 ml volume of solution remains. The clear supernatant liquor is decanted off into another vessel in order to separate it from the heavy whitish sediment (LiBr, Li + liquor entrainment). It is then cooled to -35°C. The heavy crystalline mass is filtered,

sucked dry and swept with dry nitrogen for 25-30 minutes. For analysis of dry product, see Table I, E.

Lithium Bromide Monoetherate, $\text{LiBr}(\text{C}_2\text{H}_5)_2\text{O}$

The monoetherate is prepared by the following procedure:

To 7 grams (1.0 moles) of finely cut up lithium in 350 cc of diethyl ether 74.8 grams (0.4 moles) of 1,2 dibromoethane in 200 ml of diethyl ether are added dropwise with vigorous agitation over a period of three hours. The reaction mass is then warmed up to a gentle reflux for an additional one hour. The reaction is complete when no more evolution of ethylene is observed. The reaction slurry is then filtered through a fluted paper filter. The clear, colorless filtrate is 1.65 N in lithium bromide, which represents a 91 percent yield.

The clear solution is then concentrated to approximately half its volume by distillation of diethyl ether in a stream of dry nitrogen. The resulting clear supernatant is decanted from a small amount of heavy sediment and then cooled to -70°C . The resulting crystalline solids of lithium bromide monoetherate are filtered off, washed dry and further dried in the dry nitrogen sweep for a period of 30-35 minutes. Yield 56 grams.

Analyzed samples were found to contain 49.32 and 49.80 percent Br, $\text{LiBr} \cdot 0(\text{C}_2\text{H}_5)_2$. Theoretical 49.69 percent Br; Also from analysis 1 mole of lithium bromide is combined with 1.01-1.08 moles diethyl ether. The monoetherate is easily dissolved in ether; the saturated solution at room temperature was found to be 1.8-1.9 N in lithium bromide. Upon further drying of the lithium bromide monoetherate crystals by heating to $50-60^\circ\text{C}$ it is possible to remove ether and obtain pure lithium bromide in the form of dull white, heavy powder.

Found % Br 91.40, 91.81

LiBr calc. % Br 92.05

It is interesting to note that anhydrous LiBr obtained in this manner is quite hard to dissolve in ether.

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Translated by:
V.V. Levasheff
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